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THE PENNSYLVANIA STATE COLLEGE
SCHOOL OF ENGINEERING
DEPARTMENT OF MECHANICAL ENGINEERING

THE EFFECT OF CERTAIN REAGENTS ON THE NITRIDED CASE

A Thesis
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Submitted in Partial Fulfillment for
the Degree of
MASTER OF SCIENCE
in
Mechanical Engineering

APPROVED: ____________________1932

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I. INTRODUCTION

1. The Nitriding Process.

Nitrification of steel was first given serious attention about 1911, at Watertown Arsenal, where the hard white layer formed on the bore of guns after repeated firing, was observed and studied. (Reference No.1) Prior to this, the iron-nitrogen diagram and the effect of nitrogen as an impurity in iron and steel had been investigated. (Reference 12, page 84.)

The surface-hardening properties of nitrogen with iron and its alloys having been established, investigations were carried out to develop a process which would be of commercial use. (Reference 3). Ammonia gas and liquid or gaseous cyanide have so far proved the only practical sources of nitrogen for the process. In 1913, Adolph Machlet, of the American Gas Furnace Company, received a patent on the nitriding of ferrous materials by heating the ferrous alloys in the presence of ammonia gas. (Reference 10.)

Substantially the same as the present day process, Machlet's patent provided for the passing of ammonia gas over the material to be nitrided at a temperature of above 900°F., at which temperature ammonia dissociation takes place, the nascent nitrogen diffusing into the surface of the metal. Great surface hardness was produced by Machlet's process, but the case obtained was extremely brittle, thin, and spalled badly, not only in service, but during the process of nitriding. It was evident that nitriding would not prove to be of commercial value until a satisfactory material was developed, and investigation went on with this aim in view.

In 1925, commercial application first became feasible with the development by Dr. Adolph Fry of the Krupp Works of a special steel of high chrome-aluminum content, to become known in this country as Nitralloy, (Reference 10 and others). In toughness, depth of case produced, and resistance to spalling it was far superior to any previously developed nitriding material, and was fully their equal in surface hardness. Since this important discovery, no completely satisfactory substitute for Nitralloy has been found, although certain chrome-vanadium steels have been advanced, and have been nitrided with fair success. (Reference 5).

The nitrided product has the hardest known steel surface, varying from 800 to 1200 Brinell and above. In addition to the natural wear-resistant quality imparted by its extreme hardness, it has a characteristic ability to resist chafing or seizing; nitrided bearing surfaces have been in rubbing contact without lubrication and under high pressure for long periods without wear or other ill effect. It has excellent corrosion-resistant qualities except against chlorine, mineral acids, and a few other agents, experiments indicating that at elevated temperatures it is attacked by tetra-ethyl lead. In almost every other way, it is the equal of stainless steel. It has been stated that its hardness is unaffected by heat up to a temperature of 950°F. and retains 60% of its full hardness after exposure at 1500°F. This gives nitrided steel some use as a heat-resistant alloy, and especially recommends it over carburized steel, which is a poor heat resistant. A further important advantage of nitriding over carburizing is the comparative simplicity of heat treatment, which with the lower temperature involved results in almost no distortion. This permits the hardening with safety of shapes too complicated for the carburizing process, and also permits the shop to finish machine many articles before nitriding.

2. Object of Investigation

The primary object of this investigation was to determine if introduction of various reagents during the nitriding process would result in a measurable improvement in the case obtained, either by removal of the dissociated hydrogen, or by catalytically increasing the dissociation of ammonia, or by a combination of the two. Positive results, if obtained, would be in accordance with other recent investigations, which indicated that the only objection to high dissociation was the presence of free hydrogen in sufficient quantity to cause its absorption by the specimens , resulting in an unsatisfactory case.

Various nitrogen-bearing compounds such as aniline, pyridine, and nitric oxide, have, when introduced with the ammonia, resulted in improved cases. (Reference 13). The supposed effect of these is to increase the available nitrogen. A similar desirable effect should be obtainable if the unwelcome hydrogen component of the dissociated gas were reduced. Several hydrogen removers have been tried among which were copper gauze or plating (Reference 13) and palladium scrap (Reference 8). Improvement in case was noticed when copper gauze or plating was used, but the other gave inconclusive results. With the object in mind of continuing this research, five compounds, four of which were potential hydrogen removers, were selected for study. There were two principal reasons for their choice; first, that a beneficial reaction was theoretically possible, second, the material was cheap and commercially available. These compounds were; Sodium cyanide, Aluminum chloride, Chlorinated lime (Ca O Cl) and Sodium and Potassium carbonates. In further discussion, these compounds will frequently be referred to as "catalysts". It is recognized that none of them are true catalysts, but the term is used for want of a better one. However, their effect may be considered catalytic in a broad sense, because each was used in hope of producing a definite improvement by means of a secondary reaction.

Results obained with each are discussed and shown in tables, photomicrographs, and hardness-depth curves.

II. APPARATUS

1. Nitriding Furnace.

The furance constructed for use in the investigation is shown photographed in Figure 1. The ammonia tank was connected through a needle valve and rubber tubing to a manifold, from which separate leads are taken to each furnace tube. The furnace consisted of four large plate heating units, made by Multiple-Unit Furnace Company, arranged in the form of an open-ended box, heavily insulated with "nonpareil" brick and powdered diatomaceous earth, all joints and crevices being sealed with alundum cement. The five nitriding containers were heavy nickel tubes, one inch internal diameter, with about six inches at each end exposed, and projecting outside of the furnace through fitted holes in the furnace brickwork. There was sufficient temperature drop along the exposed portions of the nickel tubing to permit the use of rubber tube stoppers without requiring artificial cooling to protect the rubber. Temperature control was provided by a hand rheostat in series with the heating coils. Ammonia gas entered the tubes from the manifold, passing first over the catalyst, then over the specimens to be nitrided, then finally discharging through tubing into a large water jar, five inches of water being maintained as back pressure on all tubes.

2. Temperature Measurement.

Five thermocouple holes were bored in the front brickwork, and a series of runs was made for temperature calibration. These runs indicated that tube temperatures over the six inch central range used for nitriding had a maximum variation of 15° C. for all five tubes over the normal nitriding temperature range (900° - 1300°F.), and that, therefore, a single temperature recording, obtained by a single thermocouple and potentiometer, was sufficiently accurate. This thermocouple was habitually placed in the central thermocouple aperture unless there was an unused tube, in which case, it was placed in the center tube, with its junction at the midpoint of the nitriding space.

3. Flow Measurement.

A glass orifice meter was mounted near the furnace with tubing so arranged that it might be quickly connected between any one tube intake and its manifold valve. This meter was carefully calibrated prior to the actual investigation by holding the pressure drop as indicated in a kerosene column a constant, ammonia being discharged through the orifice into a measured quantity of standard sulphuric acid solution to which a few drops of methyl orange had been added. Ammonia was allowed to flow at this fixed rate until neutralization occurred, and the weight of ammonia thus determined was converted into liters per hour at atmospheric conditions and room temperature. Six different rates of flow were obtained and a curve of liters per hour against centimeters of kerosene plotted. It was found desirable to leave the flowmeter permanently connected to one tube, regulate its manifold valve to the desired rate of flow, then adjust the other tube manifold valves to give the same rate of bubble flow at the discharge bottle.

4. Dissociation Measurement.

This apparatus consisted of a standard dissociation pipette manufactured by the Ludlum Steel Company. This instrument is based on the extreme solubility of ammonia in water. A measured volume of the gaseous products are taken from a discharge line of one tube and introduced into a graduated chamber. Water is then allowed to flow into the chamber, entering until it has absorbed all the undissociated ammonia. The dissociation in percent is then read directly from the waterlevel on the chamber graduations.

Dissociation was habitually measured on the tube in which no catalyst was used.

5. Hardness Measurement

The 4 kilogram Herbert Pendulum Hardness Tester with Universal Ball Vise used in this investigation is shown photographed in figure 2. This instrument measures hardness of thin cases with relatively high accuracy.

Time tests of hardness were taken on specimens of all runs at every eight hundredth of an inch of depth.

6. Weight Measurement.

Specimens of three runs were weighed on a standard Becker analytical balance to the nearest milligram before and after nitriding. Another series of weight measurements was taken, specimens being heated to 450° F. for thirty minutes, and weighed before and after heating, to determine the relative hydrogen absorption during nitriding.

7. Determination of Quality of Case.

A Rockwell "no load" test was applied to a specimen of each run. The "no load" test was carried out in accordance with the methods used by Mr. Robert Sergeson of the Central Alloy Steel Corporation, in the course of his extensive research in the nitriding field, and discussed by him in Reference 6.

Rockwell impressions were obtained by using the Rockwell machine with diamond cone, the usual 150 kg. weight being removed. Results of the examination of the impressions obtained are tabulated qualitatively.

8. Material Used.

The material used was 1" x 1/2",bar stock. Nitralloy "G", received in the heat treated sorbitic condition from the Ludlum Steel Company. The specified analysis is as follows:

Carbon	.36
Manganese	.51
Silicon	.27
Aluminum	1.23
Chromium	1.49
Sulphur	.01
Phosphorous	.013
Molybdenum	.18

The bars were first ground on a surface grinder on both flat sides. The bars were then given an accurate taper of 1/16" on their inch of width, cut up into 1/2" lengths on a milling machine and finish ground on the surface grinder. The finished specimens as ready for the furnace were then wedge-shaped blocks 1" in length and 1/2" in width with height tapering from 1/2" to 7/16" at the smaller end, the taper being 1/16" ± .002" per inch of length.

After the nitriding operation, the tapered surface was ground down on the surface grinder till the taper was removed, except for a small coupon at the small end, the final dimensions of the nitrided specimens being 7/16 x 1/2 x 1". Measuring from the inner edge of the coupon, which marked the beginning of the ground case, every 1/50 inch of length along the ground upper surface represented a case depth of 1/800 inch.

Hardness of the material as received from the Ludlum Steel Company ranged from 355 to 380 Brinell, as determined by Herbert and Rockwell tests. Other physical properties were not investigated.

III. PROCEDURE.

1. Choice of Nitriding Conditions

(a) Rate of Flow.

During the preliminary stages of the investigations, it was discovered that the practical limits of ammonia flow were from 4 to 16 liters per furnace tube per hour. Higher rates, when attempted, blew out stoppers or rubber tubing, ruining a run; lower rates were difficult to keep equalized between the various tubes. Within the above limits, the flow as indicated by meter reading on the control tube and bubble flow in the others was maintained fairly constant, the amount of fluctuation during a run being shown in the tabulations on the depth-hardness diagrams.

(b) Dissociation.

It was originally intended to take dissociation readings on all tubes, but this could not be done with a single dissociation gauge. It was, therefore, kept permanently connected to the control tube, as was the flowmeter.

Dissociation was found to be quite high, the lowest percentages obtained being 25% at 950° and 45% at 1250°. This was probably due to the relatively large area of heated nickel surface. At low rates of flow, dissociations as high as 95% were observed.

(c) Time of Run

All runs were 24 hours in duration. Such a time was about the minimum which would insure a case of measurable characteristics.

(d) Temperature.

Runs were made at temperatures of 850° and 1250°F., with one exception. These temperatures were chosen as representative of low and high temperature nitriding conditions, respectively.

Run number four, the duplex cycle, was started at the lower temperature, and the heat raised twice during the run, as indicated in the temperature-time diagram of figure six.

(e) Catalysts.

Catalysts were used in the powdered form. Except in the case of sodium cyanide, approximately 50 c.c. of the catalyst was fed into each tube at the entrance or manifold end, just clear of the rubber stoppers, and leveled off to permit free passage of ammonia. Temperatures over the catalyst section probably did not exceed 600°F.

About 5 c.c. of sodium cyanide were spread in a porcelain boat and placed in the tube. Even this small quantity produced dangerous pressures, blowing out the rubber stoppers several times. Because of the danger of cyanide gas, only one run was made with sodium cyanide.

2. Method of Conducting Runs.

The procedure used was as follows:

The furnace was brought to the desired temperature by means of the hand rheostat. Ammonia was then turned on at the tank stop valve, and by the manifold valves to all tubes in use, rate of flow being approximately adjusted by flowmeter and bubble rate. Stoppers were then removed from the entrance ends of each tube in turn, the desired catalyst added, and the stoppers replaced. After a few minutes to insure that all air in the tubes had been replaced by ammonia, the exit stoppers were removed, the specimens inserted and pushed to the center of the tube with a measured rod. The tubes were then tightly closed, and flow rate accurately adjusted.

Until steady conditions obtained, frequent readings were taken of temperature, rate of flow, and dissociation, and adjustments made in flow rate as necessary. After conditions became constant, readings were recorded at regular intervals, generally every four hours, till the end of the run. After the run, tubes were removed from the furnace to cool but were kept closed, and ammonia allowed to flow at a reduced rate, to prevent oxidation of the specimens.

IV. RESULTS AND CONCLUSIONS.

1. Effect of Use of Catalysts upon Hardness and Depth of Case.

Five runs were made with this study in view, and the results plotted showing Herbert pendulum readings against depth for all specimens in Figures Three to Six. Instead of smooth curves, point to point lines were drawn, showing the exact readings obtained. The reason for this construction was that the frequent striking similarity between slopes of corresponding portions of different "curves" as shown in these figures might prove of possible significance.

Results can perhaps be discussed more clearly if each catalyst is considered separately.

Sodium cyanide in its single appearance gave a distinct and uniform increase in hardness. It also showed the most marked increase in case depth of any of the catalysts. This was especially gratifying in that the run with this catalyst was interrupted by several small explosions, during which a large part of the active reagent escaped as cyanide gas. It is regretted that further investigation of this and other cyanides was inadvisable on the type of apparatus used.

Sodium carbonate gave a good increase in hardness, its effect being greatest at the lower temperature range and least at the higher. The effect on depth of case was negligible for all three runs.

Calcium carbonate gave results the reverse of the sodium salt, giving excellent hardness increase at high temperature with decreasing effect with reduced temperature. Effect on depth of case was slight.

Aluminum chloride at lower temperatures materially increased not only the maximum hardness, but the depth range over which high hardness was observed. There was a marked falling off of this effect at the higher temperature.

Chlorinated lime showed the most consistent results of any of the catalysts, giving marked hardness increase over the entire depth of case on all runs. Actual depth of case was increased at the low temperature run, but not on the others in any marked degree.

A mixture of the last two compounds was used for comparison in the fifth run. The case obtained was nearly the equal of a non-catalyst case obtained with a greatly increased ammonia flow. This is shown by the depth-hardness curves of Figure Seven.

Figure Nine shows the results of run number four plotted on a semi-logarithmic scale after the method advanced by George M. Eaton (Reference 11). This method demonstrates more exactly the relative wear resistance that might be expected from the various specimens.

Hardness Readings as actually obtained are shown tabulated in Table I.

TABLE I. - BRINELL HARDNESS VS. DEPTH

Depth in Inches	Run #1 - 950° F.				Run#2-950°F.			Run # 3 - 1250°					Run #4 Duplex					Run #5-1250°		
	Control	Na CN	$Na_2 CO_3$	$Ca CO_3$	Control	CaOCl	$AlCl_3$	Control	Ca O Cl	$Al Cl_3$	$Na_2 CO_3$	$Ca CO_3$	Control	$Ca CO_3$	Na_2CO_3	$Al Cl_3$	Ca O Cl	Control 5 liters flow	Control 14 liters flow	$CaOCl+ AlCl_3$
.000	710	860	700	830	760	900	780	750	840	750	750	850	850	940	900	880	880	750	750	800
.00125	850	1000	820	980	500	1180	1140	760	855	760	760	880	900	960	1020	1050	1020	770	800	810
.0025	800	930	980	815	1020	950	1210	660	865	840	720	860	980	960	1100	1060	1020	800	800	860
.00375	610	890	1040	600	900	850	970	630	780	740	720	720	850	960	1000	1000	1050	750	800	820
.005	460	680	570	515	525	750		650	760	720	680	700	830	870	910	1050	1000	680	800	750
.00625	420	660	420	490	460	550	650	650	710	700	650	610	760	850	760	900	950	650	800	750
.0075		560		450		630	580	630	650	650	650	610	610	760	760	850	860	600	790	740
.00875		530		415		550	550	610	600	630	650	600	600	750	700	830	820	570	760	700
.010							540	600	680		650	610	550	620	500	680	650	570	710	700
.01125							450	590	650		650	600	500	560	500	520	510	600	720	750
.0125							410	580	630	610	600	600	450	500	470	470	420	600	690	670
.01375								560	580		550	590	410	400	440	450	400	560	700	550
.015								560	550	610	540	610						560	650	550
.01625								570	600		540	600						530	600	580
.0175								520	570		550	600						539	600	560
.01875								520	560	560	540	600	390	400	400	390	390	490	550	500
.025								520	550	530	500	500						450	520	450
.03125								420	410	510	410	500						440	480	430
.0375										450		450						400	460	400
Case	470	370	380		390	380	400	410	410	420	410	380	390	380	400	380	390	380	415	390

2. Effect of Increase in Rate of Flow Upon Hardness and Depth of Case.

These results are taken from runs 1, 2, and 5 and are shown in Figure Eight. They indicate that increased rates of flow at both high and low temoeratures result in increased maximum hardness and total range over which the harder case exists. This is in variance with the results obtained by Robert Sargeson, who stated in his "Investigations in Nitriding" (Reference 6), that increase in flow resulted in deeper and harder cases at the higher temperatures, but had little or no effect at 950°.

3. Effect of Use of Catalysts upon Increase in Absorption by Weight.

To determine whether the presence of a catalyst caused an increase in the weight of absorbed nitrogen, three runs were made, one at low temperature, one at high, and one duplex cycle. The results are tabulated below, and generally indicate that the use of a catalyst is accompanied by an increase in weight of absorbed gas, except in the case of aluminum chloride, which for some reason brings increased hardness without increased total absorption. It must be remembered, however, that only two surfaces of each specimen were prepared for nitriding and variations in surface conditions of the four unpolished surfaces on each specimen might cause large differences in the effective area exposed to nitriding. Larger specimens more carefully prepared should give more consistent results.

TABLE II.

	Run #1 - 950°		Run #2 -Duplex		Run #3 - 1250°	
Catalyst	Increased weight in grams.	% Increase over Control	Increased weight in grams	% Increase over Control	Increased weight in grams	% Increase over Control
Control (no Catalyst)	.014		.039		.061	
Na_2CO_3	.018	28.3%	.048	25.6%	.079	29.5%
$Ca\ CO_3$	.024	71.7	.064	64.1	.077	27.9
$Al\ Cl_3$	.016	14.3	.039	00.0	.052	-14.8
Ca O Cl	.024	71.7	.076	94.9	.077	27.9

4. Effect of Use of Catalysts upon Quality of Case.

All specimens were given the no-load test in the Rockwell machine with diamond cone and the impressions examined by microscope. Amount of spalling observed on each is tabulated below.

TABLE III.

	Spalling Observed				
Run No. and Temp.	1-950°	2-950°	3-1250°	4-Duplex	5-1250°
Catalyst					
None	None	None	Much	None	Moderate at 5 liters None at 14 liters
NaCN	None				
$Na_2 CO_3$	None		None	None	
$Ca CO_3$	None		Very Slight	Slight	
Ca O Cl		None	Slight	Moderate	None
$Al Cl_3$		None	None	Much	

These results, while inconclusive, indicate that the increased hardness imparted by the catalytic agent was not accompanied by a definite increase in case brittleness.

It is of interest to note that spalling tendency seems to accompany the higher nitriding temperatures.

5. Effect of Use of Catalysts on Microstructure.

After completion of Herbert pendulum tests, specimens were given a final polish and etched. The effect of the original taper was to produce a greatly exaggerated depth of case. Specimens that had been nitrided at high temperature had apparent cases extending half their length, and five distinct layers were easily visible, the first white, the others receiving different colors in the etching process.

No distinct change in structure attributable to the use of catalysts could be observed under the microscope. There seemed to be a slight increase in the coarseness and in the white areas in the specimen that had been nitrided in the presence of a catalyst, but even at very high power the difference was not sufficient to preclude the possibility of error due to slight difference in amount of etch, or in locating corresponding regions on different specimens.

The hard spot of each specimen as determined by the Herbert pendulum was located, and upon microscopic examination, was found to be at or very near the transition point between the white outer layer and the adjacent dark layer. It was assumed, therefore, that maximum hardness occurred at this transition point, and photomicrographs were taken of this region on the control specimens of runs two, three, and four, and on the specimens which showed maximum hardness of the same runs. These photomicrographs are appended (Figures 10-15).

4% Nitric acid was used as the etching reagent as giving more satisfactory results than any other of several reagents tried. The visual etched case was identical with that indicated by the Herbert pendulum.

6. Conclusions.

The results of this investigation indicate that the hardness of the nitrided case is considerably increased if a small quantity of any one of several compounds, or catalysts, is introduced into the furnace so as to come in contact with the ammonia gas at or near the region where dissociation begins. These compounds are sodium and calcium carbonates, sodium cyanide, aluminum chloride, and chlorinated lime. Chlorinated lime gave the most consistent improvement, although beneficial results were observed with all.

This hardness increase is accompanied by a slight increase in case depth, and with the possible exception of aluminum chloride, increase in the total weight of absorbed gases. There was no marked change in microstructure and, as far as the Rockwell test would show, no positive loss in quality of case.

Results also indicate that increase in ammonia flow produces increased hardness and case depth, over the entire temperature range.

The effects of the various catalysts are beyond the writer's ability to analyze. A possible explanation is that in the early stages of nitriding operation, the catalyst reacts with the dissociated hydrogen, perhaps disturbing the equilibrium point and causing further dissocation. The material to be nitrided is subjected to a concentrated atmosphere of nascent nitrogen, and nitriding proceeds under optimum conditions. The absorption of hydrogen decreases after some time, as the catalyst loses its strength, and the nitriding atmosphere approaches a usual composition. During the early period, however, the material being nitrided has built up a thin nitrogen-saturated surface which resists the absorption of the hydrogen, but permits nitrogen to enter as the case deepens. The early formation of the ideal surface with the assistance of the catalyst causes conditions that favor an improved case during the entire run. This is in accordance with the theory advanced for the hard, deep case obtained on the duplex run, which suggests that the low temperature at the start of the run causes the selective absorption of nitrogen, forming a thin hard case, and this surface condition decreases later absorption of hydrogen, even at the higher and more favorable temperatures.

V. RECOMMENDATIONS - ACKNOWLEDGMENT.

It is realized that the results obtained in this investigation are little more than an indication, and that much important data was incompletely determined or was entirely neglected. Limitations of the apparatus are partially responsible, but inexperience and insufficient time were the principal factors.

Among the items neglected in this work which should be included in further investigation are: (1) a more complete analysis and control of dissociation conditions, (2) effect of varying duration of run, (3) effect of varying amount of catalyst, (4) further micro-analysis, (5) more practical tests of case quality, (6) other catalysts.

The investigation was carried out with the facilities and hearty cooperation of the Metallurgical Department, School of Mineral Industries. Mr. J. E. Long of this department suggested the possibility of research in the field of catalysts in nitriding, assisted in the design and construction of the apparatus, and during the entire investigation. He is largely responsible for its success.

Dr. H. B. Northrup, Director of the Extension Department, School of Mineral Industries, assisted greatly during the investigation, and the preparation of this report. Professor J. O. Keller, of the Extension Department

School of Engineering, made possible the use of the Herbert Pendulum in the investigation, and assisted personally in its use. His treatise on the machine (Reference 10) was freely consulted during this phase of the work.

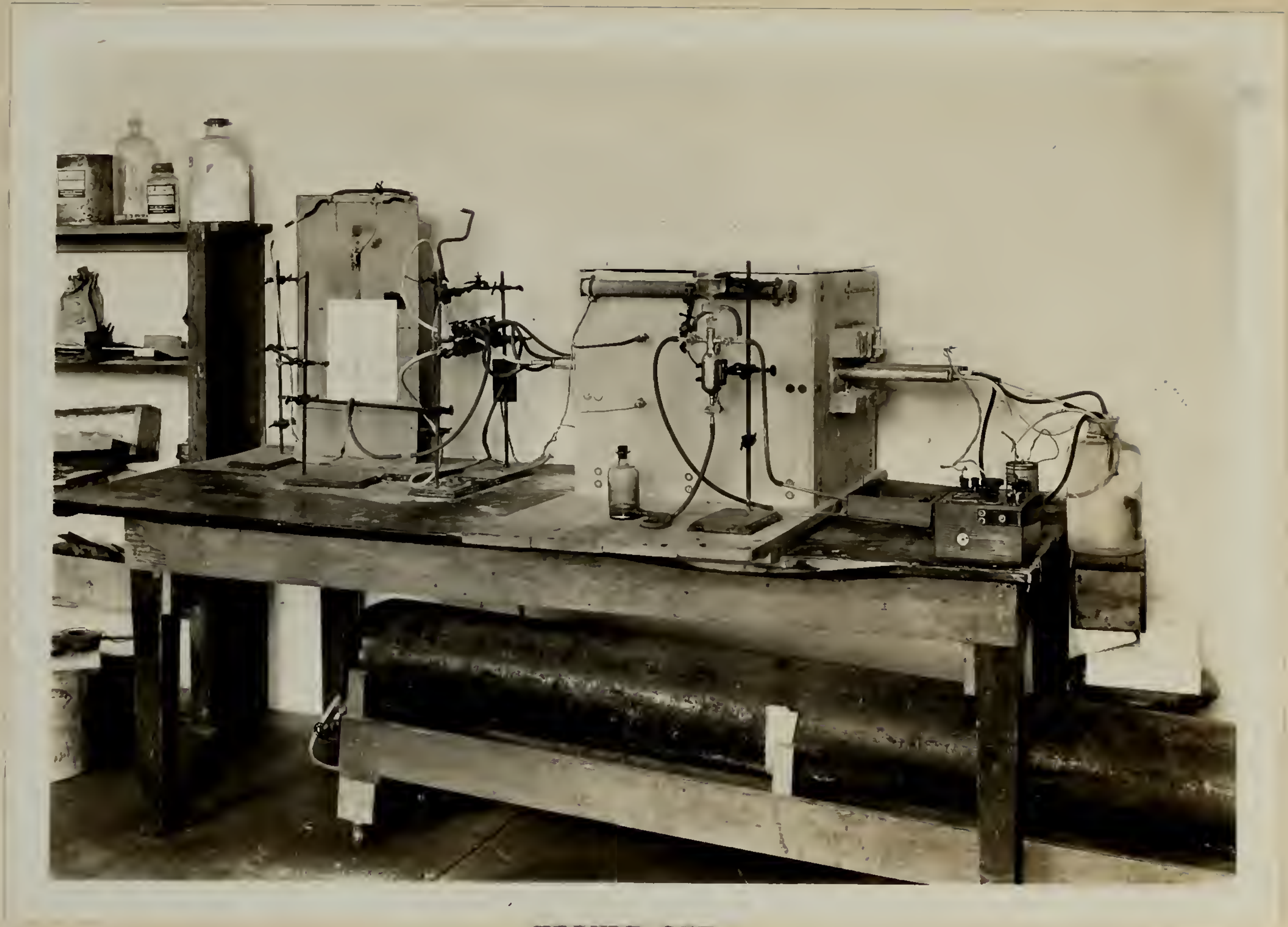

FIGURE ONE

View of Apparatus

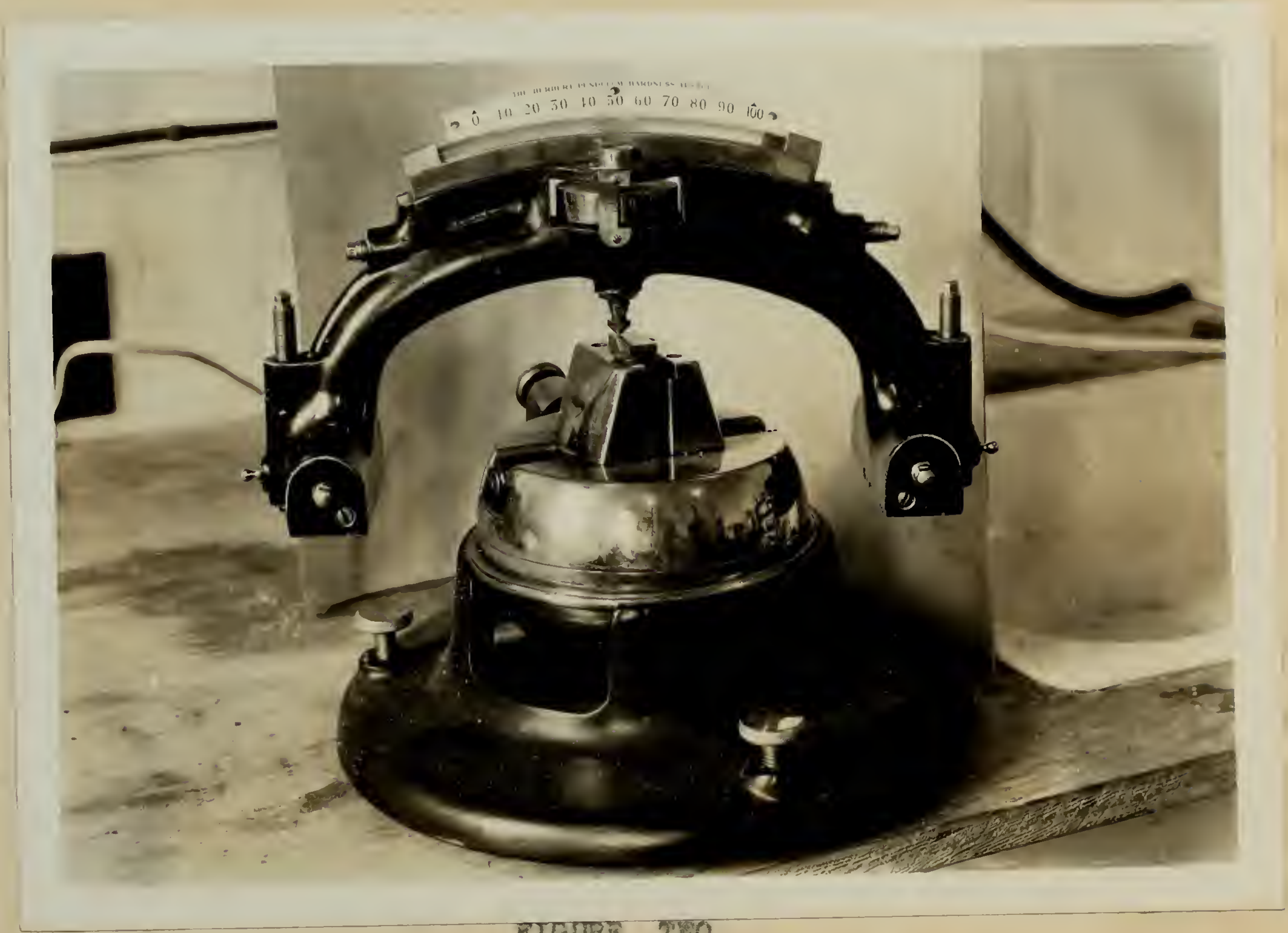

FIGURE TWO

Herbert Pendulum Hardness Tester

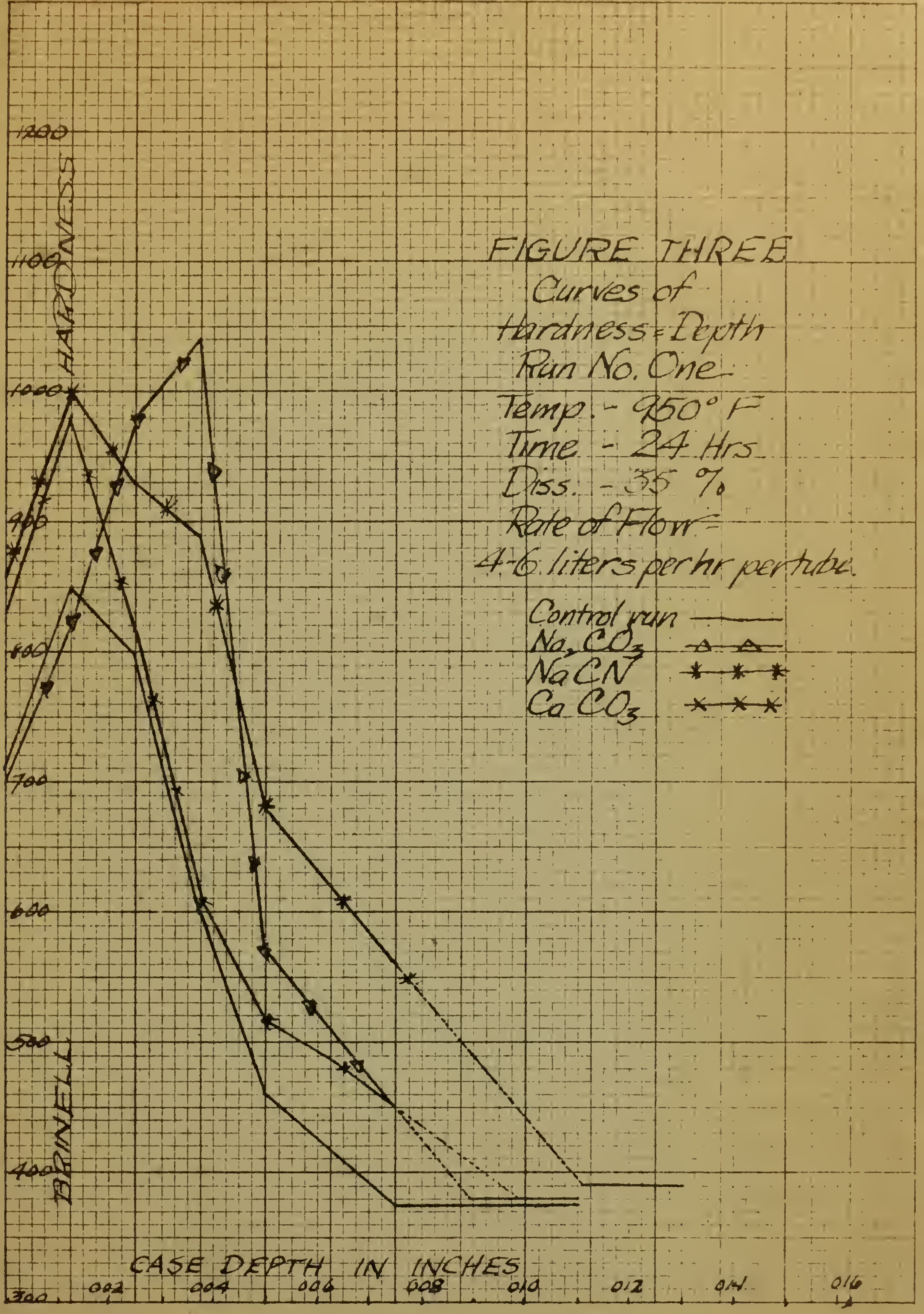

FIGURE THREE
Curves of
Hardness - Depth
Run No. One
Temp. - 950° F
Time - 24 Hrs
Diss. - 35 %
Rate of Flow =
4-6 liters per hr per tube.

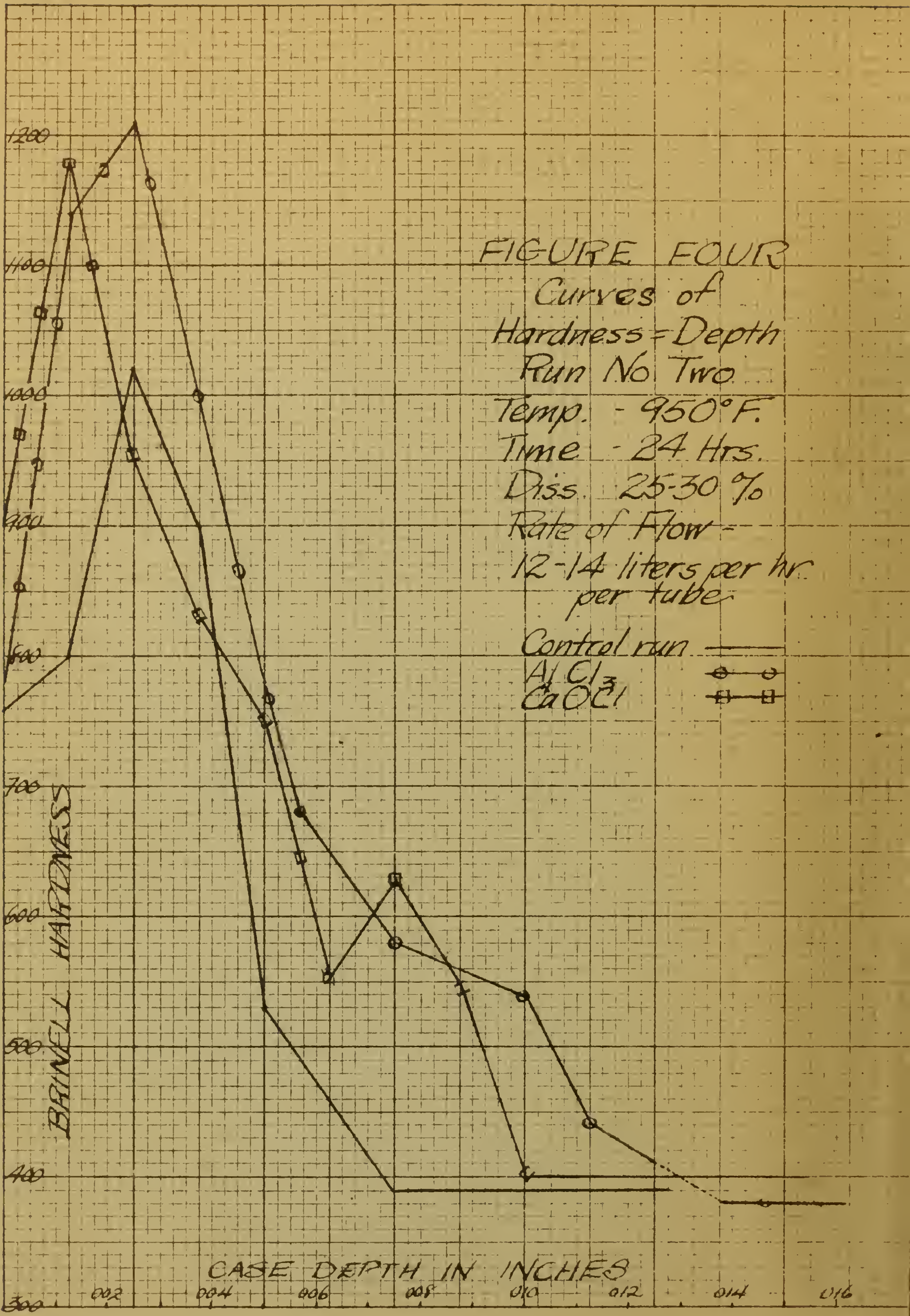

FIGURE FOUR
Curves of
Hardness = Depth
Run No Two
Temp. - 950°F.
Time - 24 Hrs.
Diss. 25-30 %
Rate of Flow -
12-14 liters per hr.
per tube

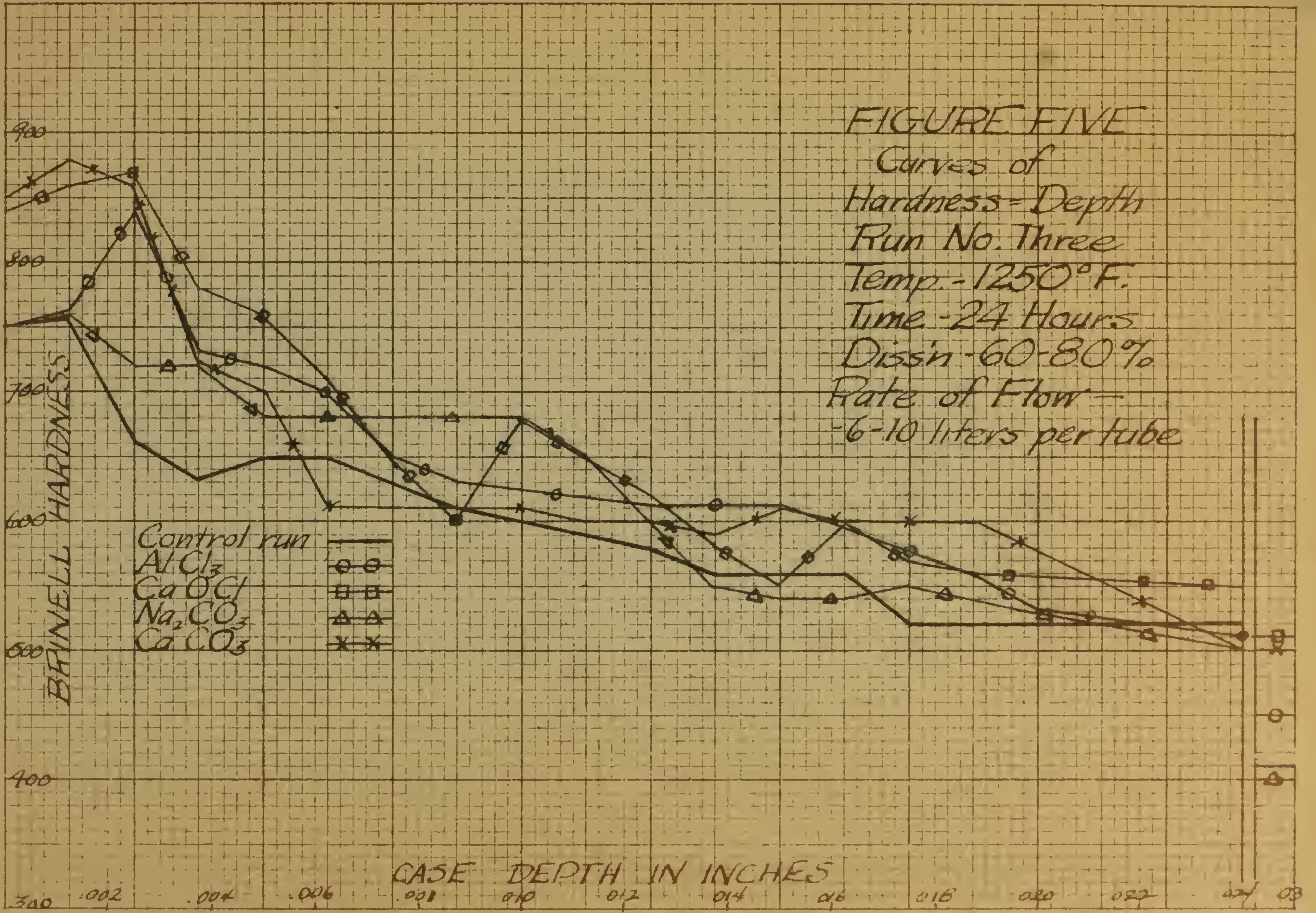

FIGURE FIVE
Curves of
Hardness-Depth
Run No. Three
Temp.-1250°F.
Time -24 Hours
Diss'n -60-80%
Rate of Flow -
-6-10 liters per tube

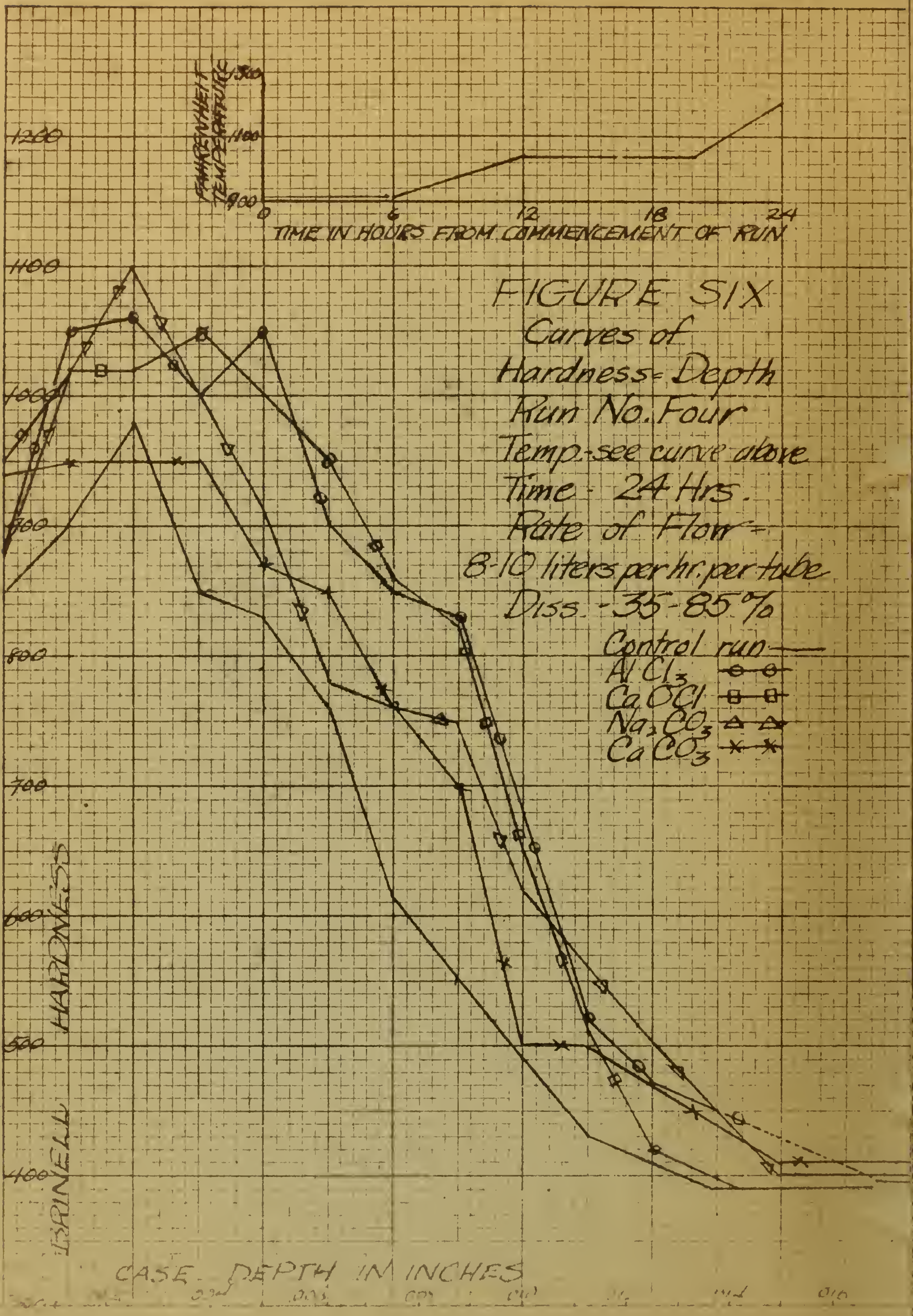

FIGURE SIX
Curves of
Hardness-Depth
Run No. Four
Temp. see curve above
Time - 24 Hrs.
Rate of Flow =
8-10 liters per hr. per tube
Diss. - 35-85 %

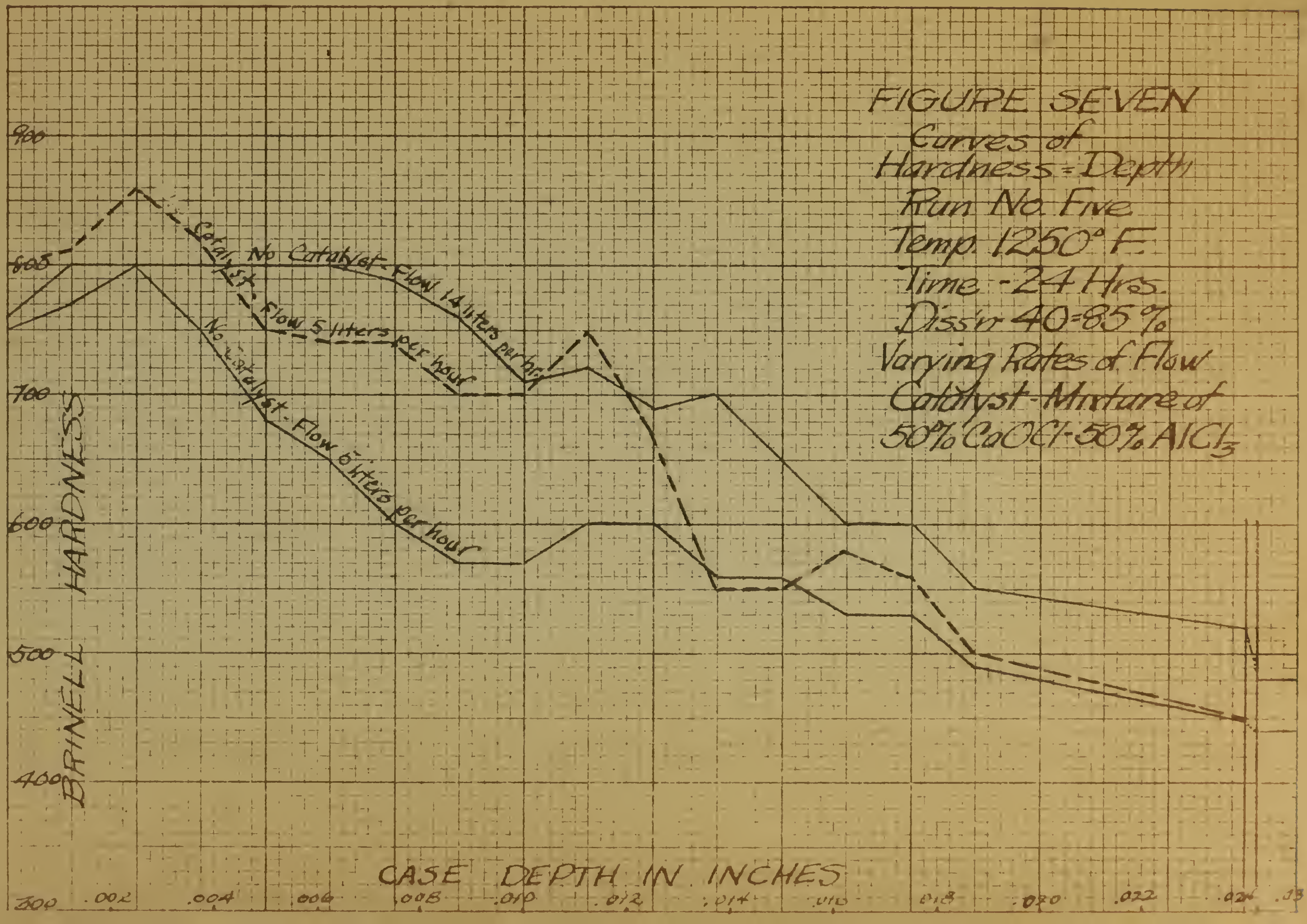

FIGURE SEVEN
Curves of
Hardness - Depth
Run No. Five
Temp. 1250° F.
Time - 24 Hrs.
Diss'n 40-85 %
Varying Rates of Flow
Catalyst - Mixture of
50% CaOCl - 50% AlCl$_3$

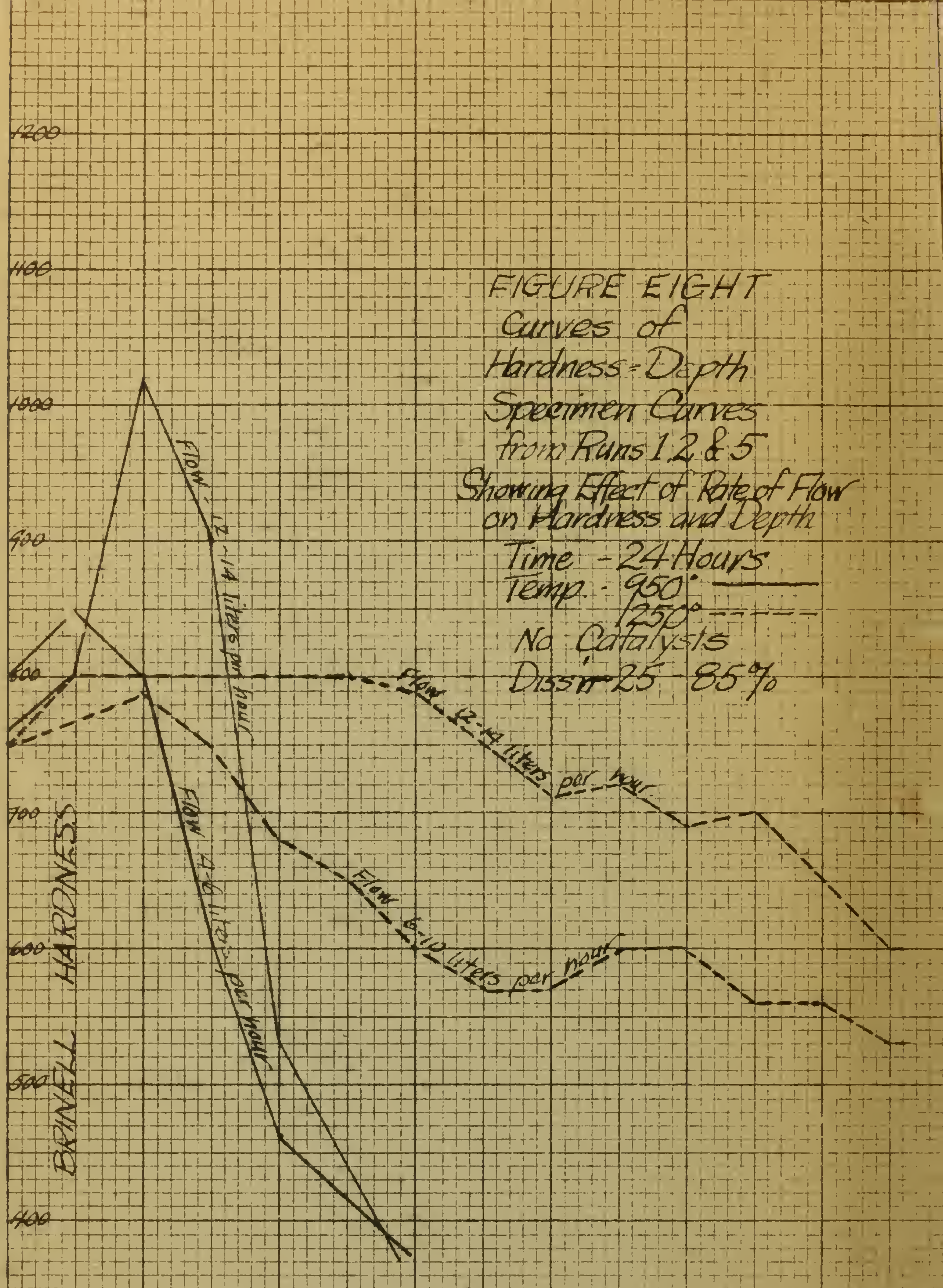

FIGURE EIGHT
Curves of
Hardness - Depth
Specimen Curves
from Runs 1, 2, & 5
Showing Effect of Rate of Flow
on Hardness and Depth
Time - 24 Hours
Temp. - 950° ———
1250° - - - - -
No Catalysts
Diss'n 25 - 85%

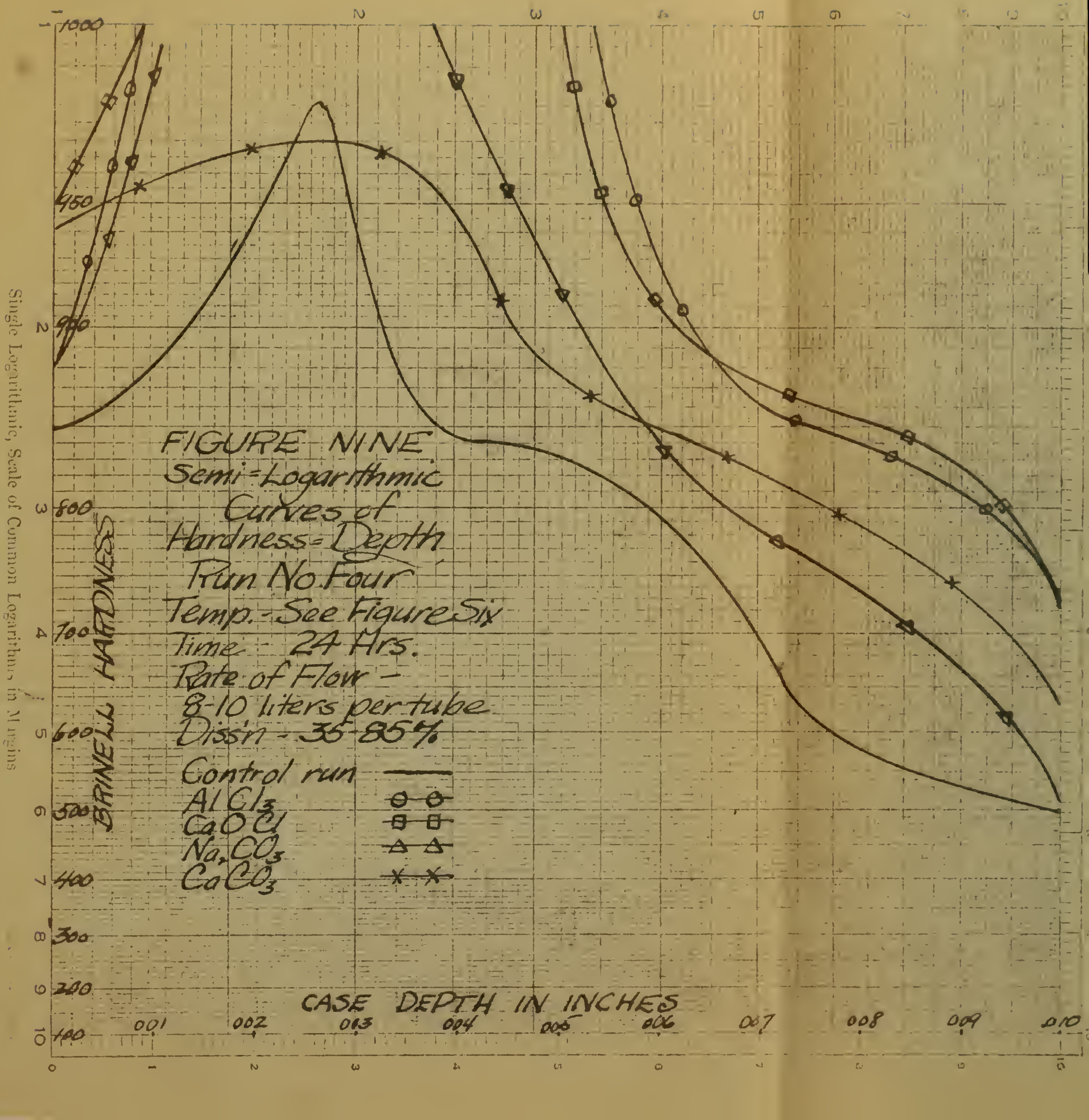

FIGURE NINE
Semi-Logarithmic
Curves of
Hardness-Depth
Run No. Four
Temp. - See Figure Six
Time - 24 Hrs.
Rate of Flow -
8-10 liters per tube
Diss'n - 35-85%

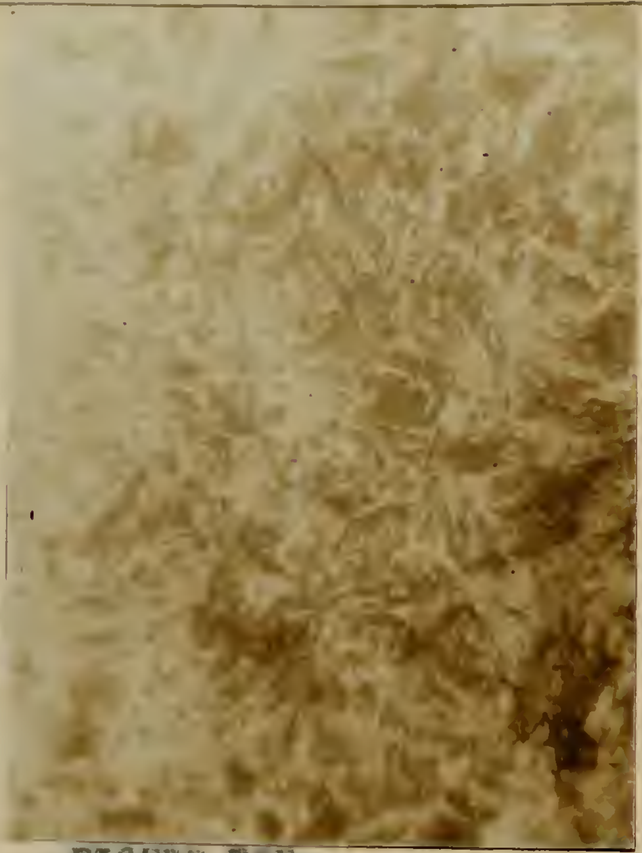

FIGURE TEN
RUN TWO
TEMP. 950°

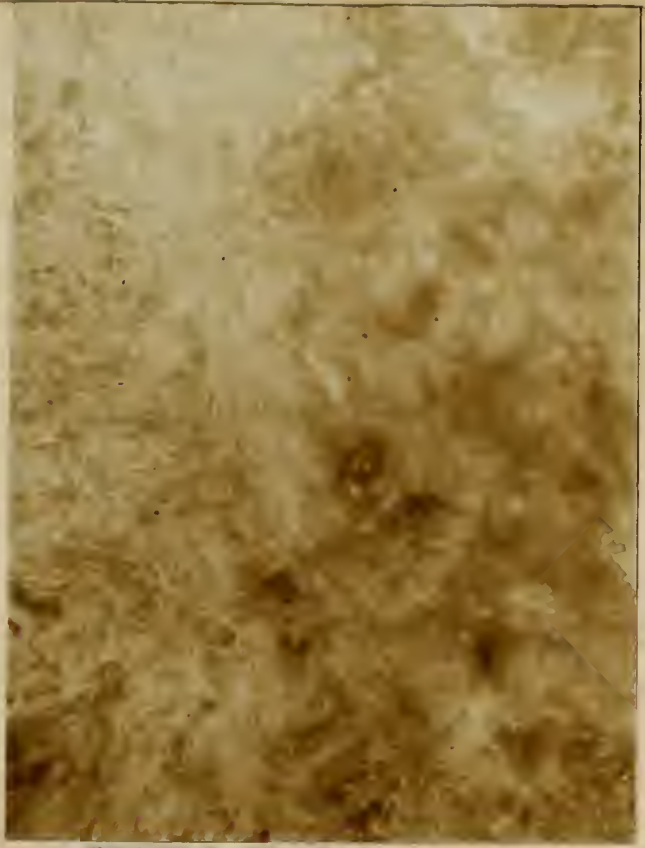

FIGURE ELEVEN
RUN FOUR
DUPLEX CYCLE

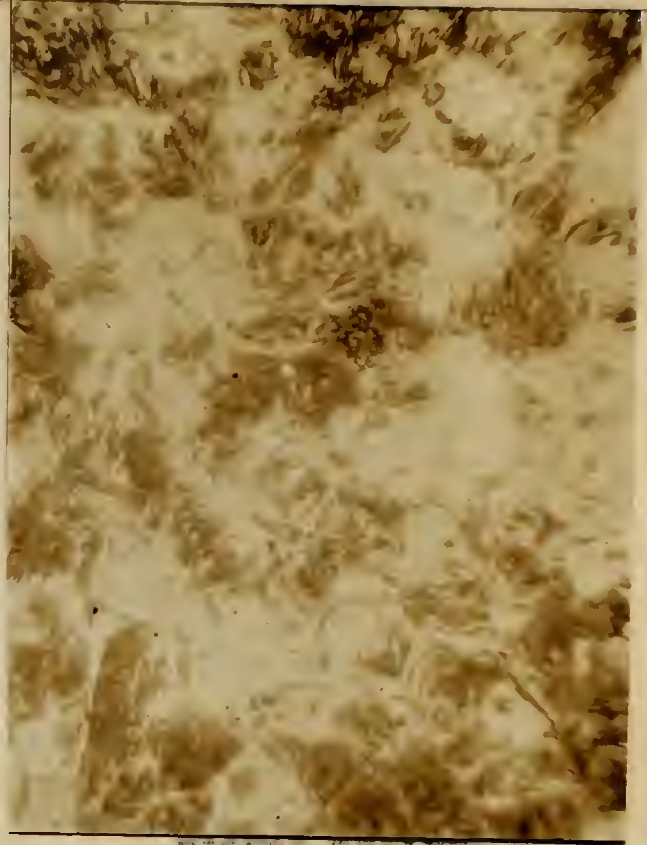

FIGURE TWELVE
RUN THREE
TEMP. 1250°

PHOTOMICROGRAPHS OF "HARD SPOTS" OF CONTROL SPECIMENS
(NO CATALYSTS) ETCHED IN HNO_3 x 500.

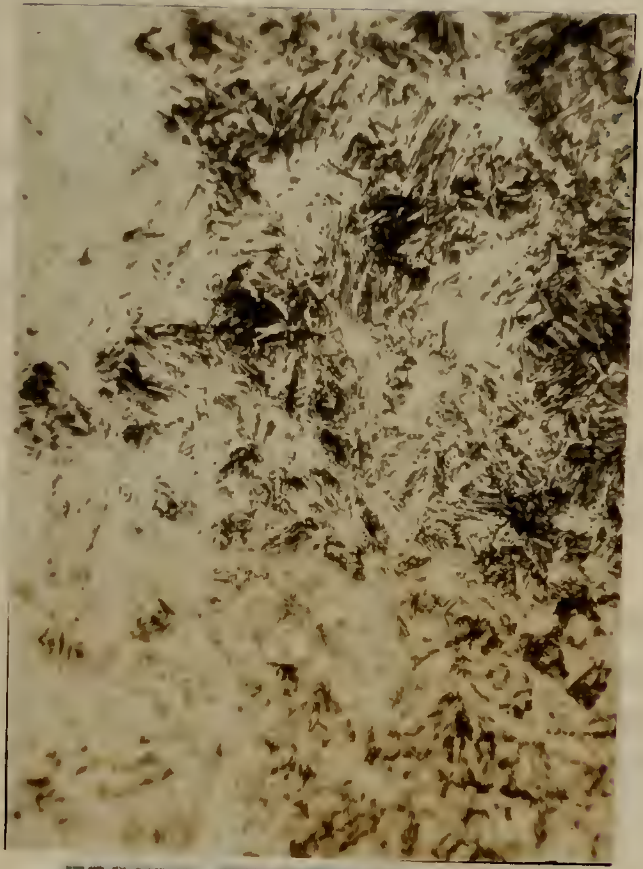

FIGURE THIRTEEN
RUN TWO
TEMP. 950°
CATALYST $Al\ Cl_3$

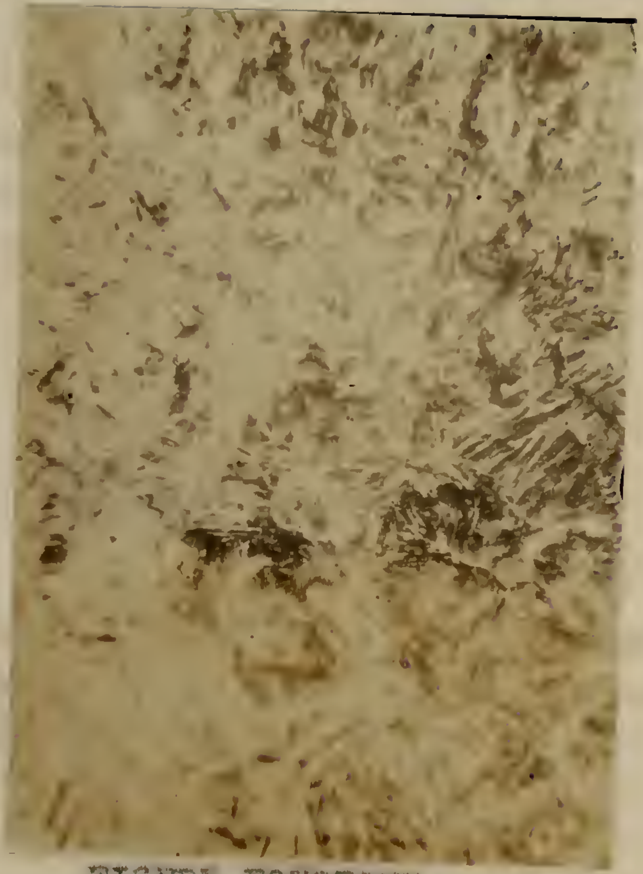

FIGURE FOURTEEN
RUN FOUR
DUPLEX CYCLE
CATALYST Na_2CO_3

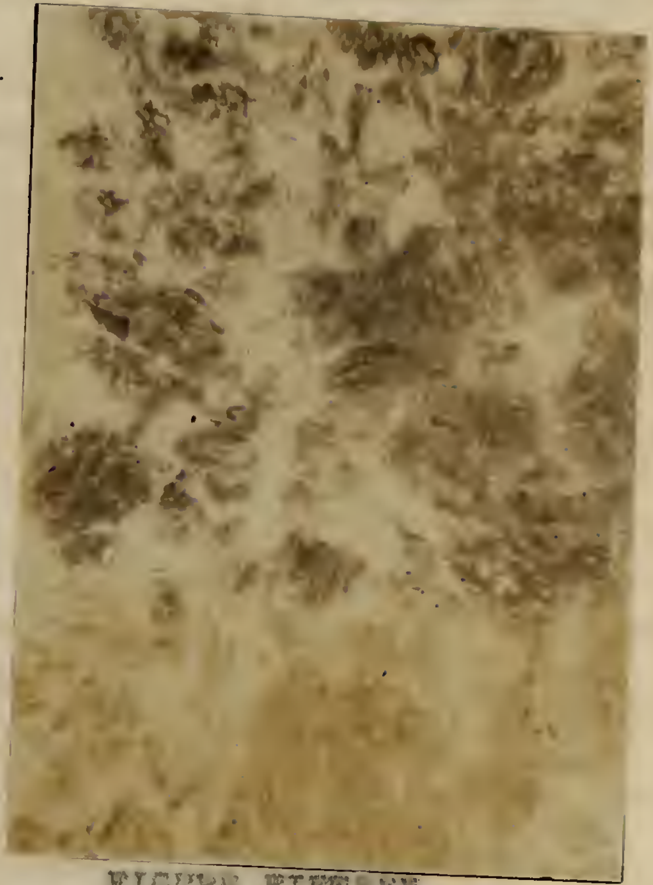

FIGURE FIFTEEN
RUN THREE
TEMP. 1150°
CATALYST $Ca\ CO_3$

PHOTOMICROGRAPHS OF "HARD SPOTS" OF HARDEST SPECIMENS.

ETCHED IN HNO_3 X 500

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